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(21) International Application Number: PCT/FI91/00111 (22) International Filing Date: 12 April 1991 (12.04.91) (30) Priority data: 901895 12 April 1990 (12.04.90) FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; P.O. Box 310, SF-06101 Porvoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only) : ALA-HUIKKU, Sirpa [FI/FI]; Korvatunturintie 5 B 7, SF-00970 Helsinki (FI). SORMUNEN, Pekka [FI/FI]; It. Pitkääkatu 22, SF-06100 Porvoo (FI). (74) Agent: BERGGREN OY AB; P.O. Box 16, SF-00101 Helsinki (FI).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>
(54) Title: PROCATALYST COMPOSITION FOR THE POLYMERIZATION OF OLEFINS, ITS PREPARATION AND USE (57) Abstract <p>According to the invention a novel procatalyst composition suitable for polymerization of olefins has been prepared. It is prepared by treating a solid carrier with (a) a magnesium halide compound, (b) such a magnesium halide dissolving transition metal compound, which contains no chlorine, and (c) an electron donor compound dissolving/suspending said magnesium halide compound. The precursor product which is obtained after the said steps (a)-(c) which are carried out in different sequences, has additionally been treated with a chlorine compound containing no transition metal, or with a mixture of said chlorine compound and an organometallic compound.</p>		

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Procatalyst composition for the polymerization of olefins,
its preparation and use

- 5 The present invention relates to a procatalyst composition which is suitable for homo- and co-polymerization of olefins.

10 The invention also relates to a method for preparation of such a procatalyst composition and its use together with an organometallic co-catalyst compound for polymerization of olefins.

15 In the polymerization of olefins a Ziegler-Natta-catalyst system generally is used consisting of a so called procatalyst and a co-catalyst. The procatalyst is a component based on a compound of a transition metal belonging to some of the groups IVA-VIII (Hubbard, IUPAC 1970) of the periodic system of the elements. The co-catalyst again is a component based
20 on an organic metal compound of a metal belonging to some of the groups IA-IIIA of the periodic system of the elements. The catalyst system usually also contains electron donating compounds which improve and modify the catalytical properties.

25 It is conventional to use in the preparation of heterogenic polymerization catalysts as a component enhancing the polymerization activity of the procatalysts a support compound, on which the transition metal compound is superposed. The
30 usual carrier compounds are based on silica, aluminum oxide, magnesium oxide, titanium oxide, a mixture thereof, carbon in different forms, and different types of polymers. As important carrier compounds have proved the magnesium compounds such as alkoxides, hydroxides, hydroxy halides and
35 halides, of which the latter, in particular magnesium chloride, have recently become the most significant carrier components of procatalyst compositions.

Because magnesium compounds and in particular magnesium halides are not activated very efficiently in their base crystal form with a transition metal compound their crystal form has to be deformed. Traditionally the deformation of the crystal form is carried out by grinding e.g. in a ball mill typically resulting in a finely divided matter with a large specific surface, the particles of which have strongly deformed crystal lattices. Drawbacks of the usual grinding method include, however, that the grinding is very energy consuming, causes wearing and corrosion of the apparatus, and is suited to the production of catalyst only with the tedious batch process.

A more modern method to provide a deformed crystal form of magnesium compounds such as a magnesium halide and thereby enhance its ability to become activated with a transition metal compound is to modify it chemically. Thereby a magnesium compound, optionally an electron donor and a transition metal compound are reacted, often in a solution, to an easily isolated procatalyst composition. Enough amorphous procatalyst is anyhow not formed in the process since the composition is more or less spontaneously crystallized in the preparation whereafter its morphology is not essentially changed.

U.S. Patents No. 4,124,532 and 4,174,429 describe the preparation of this kind of catalytically active complexes by reacting a magnesium halide and a transition metal compound at a suitable ratio in a electron donor solvent. The finished complex can be separated through crystallization by evaporation of said solvent, or by mixing the complex with a solvent in which it isn't soluble. Because such complex compounds are formed as a result of a spontaneous crystallization, their crystal structure is very regular and activity rather limited.

U.S. Patent 4,302,566 and EP Patent Application 6,110 describe a precursor formed by a magnesium halide, a transiti-

on metal compound and an electron donor. The precursor is formed by precipitation from an electron donor solution whereafter it is separated and mixed with an aluminumalkyl which is activating it and a separate inert carrier. In these processes an essentially amorphous procatalyst composition is not formed either, because the precursor in question is crystallized in the preparation spontaneously and its morphology is not essentially changed after that.

DE Patent No. 2,949,735 describes the dissolution of magnesium chloride into 2-ethylhexanol in kerosene, the addition of titanium tetra-butoxide to the cooled down complex solution and the use of the thus obtained catalyst solution together with an organic Al-chloride in the co-polymerization of ethene. Hence it is dealt with a non-supported catalyst solution, whereby a controlled morphology of the polymer particles is not obtained. The alcoholic hydroxyl groups which are deleterious in respect of the polymerizing activity are in that arrangement not either removed with a separate treatment.

EP Patent Application No. 166,970 describes the treatment of magnesium chloride with titanium tetrabutoxide in heptane, the treatment of the surfaces of the particles obtained with an organic hydroxy compound such as an alcohol, a silanol or a phenol, the treatment of the product with a titanium halide and a polymeric silicon compound.

In the latter publication a solid procatalyst composition is prepared in two titanation stages which are difficult and sensitive e.g. to impurities.

US Patent No. 4,833,111 describes suspending of a silica activated at 600°C into hexane, reacting of the surface hydroxyl groups of the silica with dibutylmagnesium, reacting of the magnesium with ethanol whereby the butyl group is substituted by a ethoxy group, and activating of the catalyst with titanium tetrachloride and ethyl aluminum

dichloride.

The latter specification has as a drawback that in it as the magnesium compound an organometallic compound is used
5 which doesn't itself carry a halogen needed in the formation of a catalytically active complex. The provision of a catalytically active interaction between magnesium and the transition metal hence requires the use of transition metal halides such as titanium tetrachloride. The sensibility of
10 this kind a reagent e.g. to the moisture in the air is in turn greatly hampering the activation of the carrier.

The purpose of the present invention is to provide a solid procatalyst composition which is as active as possible,
15 and which has a suitable particle form, particle size and particle size distribution. These objects have to be fulfilled as easily as possible and without the above mentioned drawbacks.

20 The problem has now been solved by a a novel procatalyst composition intended for polymerization of olefins, which composition is mainly characterized by what is said in the characterizing part of claim 1. It has thus been found that a useful procatalyst composition is easily obtainable by
25 impregnating a separate, inert carrier with a magnesium halide, a transition metal compound dissolving said magnesium compound and containing no chlorine, and an electron donor, and by chlorinating with a chlorine compound containing no transition metal, or with a mixture of said
30 chlorine compound and an organometallic compound. A procatalyst is thus obtained which has its chlorine/metal ratio at an optimal level in respect of the polymerization result.

The invention has as compared with the solutions of the
35 prior art as an advantage the controlled morphology of the catalyst thanks to the carrier, in particular the silica. Additionally the catalyst according to the invention has both a high activity and good hydrogen sensitivity and a

good co-monomer sensitivity and the polymers obtainable with it have a narrow molecular weight distribution.

The use of a solution of a magnesium compound, an electron donor compound and a transition metal compound containing no chlorine for the treatment of the carrier makes it possible for one thing that a separate activation step with a transition metal compound is not needed but only the chlorination is enough, and for another thing, that a magnesium halide, preferably an anhydrous magnesium dichloride can be used as the magnesium compound instead of an organomagnesium compound and thus gain advantage of its structure in the production of a procatalyst composition which is as active as possible.

In the Finnish Patent Application 89-5703 a method for the production of a solid procatalyst composition has already been mentioned wherein a solid carrier is impregnated with a mixture of a Mg compound and a transition metal compound dissolving this Mg compound, and the resulting composition is chlorinated with a compound containing no titanium. The Mg/Ti ratio used in this process is usually of the order 0.5 and it can be of at most about 1, and the obtained polymerization activity as calculated in relation to titanium is typically 100-130 kg PE/g Ti. The remaining titanium in the polymer is over 10 ppm. The difference of this invention in relation to the mentioned Finnish Patent Application is that by the use of an electron donor a desired Mg/Ti mole ratio of at least 1, preferably between 1 and 4 can be provided, and at the same time a higher activity of the catalyst per the transition metal can be obtained. Polymerization activities thus are obtained with the catalyst composition according to the invention which typically are 200-500 kg PE/g Ti and then the titanium remainders are less than 5 ppm.

The carrier to be used according to the invention can be of whatever porous inorganic or organic material. Of the

organic carriers the polymers can be mentioned. Especially preferable inorganic materials are based on oxides of silicon, aluminum, titanium, magnesium and/or chromium. Such materials are e.g. silica, aluminum oxide, magnesium oxide, magnesium silicate, titanium oxide, etc. Especially preferred carriers are silica, aluminum oxide and magnesium silicate or a mixture thereof. Most preferable is silica.

The physically bound water can optionally be removed thermally from the surface of the inert carrier by drying at a temperature under 200°C.

The surface hydroxyl groups of the carrier can optionally be removed thermally at a temperature above 200°C or chemically by using agents reacting with the hydroxyl groups. The removal of the surface hydroxyl groups is, however, not necessary for the performance of the catalyst as is shown in the examples of the specification.

Agents suitable for the chemical removal of the surface hydroxyl groups of the carrier are organic silicon, aluminum, zinc, phosphorus and/or fluorine compounds. Of the suitable organic silicon compounds as the preferred ones may be mentioned the compounds of formula $(R_3Si)_2NH$ or formula R_nSiX_{4-n} , wherein R is a hydrogen and/or an alkyl group, X is a group reacting with the H of a hydroxyl group such as a halogen, and n is 1, 2 or 3. Of the preferred organic aluminum compounds the compound of formula $[R_nAlX_{3-n}]_m$ can be mentioned, wherein R is a hydrogen and/or a hydrocarbon group containing 1-20 carbon atoms, preferably a lower alkyl group, X is a halogen, n is 1, 2 or most preferably 3, and m is 1 or 2. Typical aluminum compounds are trialkylaluminums such as triisobutylaluminum, dialkyl aluminum halides such as diethyl aluminum chloride and dialkyl aluminum hydrides such as diisobutyl aluminum hydride. Preferred phosphorus compounds removing hydroxyl groups are phosphorustrihalides, phosphorusoxytrihalides, dialkyl phosphorus halides, monoalkyl phosphorus halides and diamino

phosphorus oxyhalides. Suitable fluorine compounds removing hydroxyl groups are gaseous fluorine, hydrogenfluoride, borontrifluoride, silicon tetrafluoride and sulphuroxydifluoride.

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The most preferred agents removing hydroxyl groups are organic silicon compounds and organic aluminum compounds and of these the most preferred hexamethyldisilazane $[(CH_3)_3Si]_2NH$ and triethylaluminum $(C_2H_5)_3Al$, respectively.

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After the optional removal of at least physically bound water from the surface of the carrier it is impregnated with a magnesium halide compound, with one or several compounds of the transition metals belonging to the groups
15 IVB or VB of the periodic system of the elements, which compounds dissolve the said magnesium compound and contain no chlorine, and with an electron donor compound which is dissolving/suspending the Mg compound. It can according to one embodiment be carried out by contacting the carrier
20 with a mixture which has been formed from a magnesium halide compound, from one or several transition metal compounds of the groups IVB and VB of the periodic system of the elements containing no chlorine, and from an electron donor compound. The mixture is preferably in the form of a sol-
25 ution, especially in the form of a hydrocarbon or electron donor solution, wherein the dissolved material can be a complex formed by a magnesium compound, a transition metal compound and an electron donor compound.

30 According to an other embodiment the impregnation is carried out by adding a magnesium halide compound, a transition metal compound containing no chlorine and an electron donor compound to the carrier without separate dissolution. According to a further embodiment the impregnation of the
35 carrier can be carried out by first contacting the carrier with a mixture formed from a magnesium compound and an electron donor compound and then with a mixture formed from a magnesium compound and a transition metal compound.

Suitable magnesium compounds are the Mg halides, especially magnesium dichloride. Suitable transition metal compounds are liquid compounds dissolving the magnesium compounds. Such compounds are e.g. transition metal alkoxides such as
5 the tetraalkyltitanates (titanium tetraalkoxides) titanium tetraethoxide, titanium tetrapropoxide and titanium tetrabutoxide.

Suitable electron donor compounds are liquid organic compounds dissolving the magnesium compounds. Such compounds
10 are e.g. alkylesters of carboxylic acids, aliphatic ethers, cyclic ethers, aliphatic ketones and aliphatic alcohols. Preferred electron donor compounds are ethyl acetate and tetrahydrofuran and the most preferable are aliphatic al-
15 cohols such as ethanol, propanol and butanol.

When the carrier has been treated with a magnesium halide compound, one or several transition metal compounds containing no chlorine and an electron donor compound, the
20 reaction product or precursor resulting from the compounds and containing the electron donor, is reacted with a chlorine compound containing no transition metal or with a mixture of said chlorine compound and an organometallic compound.

Suitable organometallic compounds are e.g. organic aluminum compounds such as trialkyl aluminums, other metal alkyls
25 such as butyllithium, and organic silicon compounds such as hexamethyldisilazane. The most preferred organometallic compounds are the organic silicon compounds and organic
30 aluminum compounds, and from these hexamethyldisilazane and triethylaluminum, respectively.

The chlorine compound containing no transition metal is preferably HCl, CCl₄, silicon chloride or especially a
35 compound of formula $[R_nAlCl_{3-n}]_m$, wherein R is a hydrocarbon group with 1-20 carbon atoms, preferably a lower alkyl group, n is 1 or 2 and m is 1 or 2. Typical aluminum compounds suitable for chlorination are alkyl aluminum chlor-

ides such as diethyl aluminum chloride, ethyl aluminum sesquichloride and ethyl aluminum dichloride.

It is also possible to add the organometallic compound to
5 the carrier before impregnation of the carrier with the transition metal compound. The carrier is in that case first impregnated with a solution/sludge of the magnesium compound and the electron donor, then reacted with the organometallic compound and thereafter impregnated with a mixture of the
10 magnesium compound and the transition metal compound in a liquid form. The product obtained is finally chlorinated with a chlorine compound containing no transition metal.

The invention also relates to a method for preparing a
15 procatalyst composition of the type described above, wherein one or several inert, solid carriers are treated, from which carriers hydroxyl groups of the surface have optionally been removed thermally or chemically by reacting the carrier with a compound removing hydroxyl groups, by impregnating
20 the carrier with a magnesium halide compound, with one or several compounds of transition metals of groups IVA and VA of the periodic system of the elements (Hubbard, IUPAC 1970), dissolving said magnesium compound and containing no chlorine, and an electron donor compound dissolving/
25 suspending said Mg-compound, and treated with a chlorine compound containing no transition metal, or with a mixture of said chlorine compound and an organometallic compound.

The same definitions are valid for the method according to
30 the invention as are for the catalyst composition defined by the method.

The method is typically carried out e.g. by removing from
one or several inorganic oxides only physically bound water
35 by drying at a temperature under 200°C, or also the hydroxyl groups of the surface by calcination at a temperature above 200°C and/or chemically with an organosilicon compound, preferably hexamethyldisilazane.

A pre-mixture is prepared by dissolving a magnesium compound, most preferably anhydrous magnesium chloride, into a transition metal compound dissolving it, such as a titanium alkoxide, preferably titanium tetrabutoxide, and into an electron donor compound dissolving/suspending it, preferably n-butanol, at a temperature above 20°C. The solution is preferably in the form of a hydrocarbon or an electron donor solution.

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The Mg/Ti mole ratio can be as high as or higher than 1, preferably between 1-4. The Cl/Ti mole ratio can be about 1-10, preferably 3-5. The ED/Ti mole ratio can be between 1-100.

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The pre-mixture is added to the carrier while stirring and stirring is optionally continued for 1-100 hrs at a temperature above 20°C. The hydrocarbon and/or electron donor solution is evaporated at a temperature above 20°C until a dry, free flowing powder is obtained.

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The components of the pre-mixture can also be added to the carrier without a separate dissolution so that a magnesium compound, a transition metal compound, an electron donor and optionally a hydrocarbon solvent are mixed into the carrier, whereafter the stirring of the procatalyst can be continued at a temperature above 20°C for 1-100 hrs, and the hydrocarbon and/or electron donor solution is evaporated at a temperature above 20°C until a dry, free flowing powder is obtained.

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The impregnation of the carrier can also be carried out in two stages so that first a pre-mixture 1 is added which is prepared by dissolving a part of the magnesium compound into the electron donor compound either in a hydrocarbon solvent or without a hydrocarbon solvent, and then by adding either to the dried or undried, impregnated carrier, a pre-mixture 2, which is prepared by dissolving a part of the magnesium

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compound to the transition metal compound in a hydrocarbon solvent or without a hydrocarbon solvent. The obtained precursor is stirred and the stirring can be continued for 1-100 hrs at a temperature above 20°C, and finally the precursor is dried at a temperature above 20°C until a dry, free flowing powder is obtained.

The obtained precursor is thereafter treated with a chlorine compound containing no transition metal, or with a mixture of the chlorine compound in question and an organometallic compound. It is also possible to treat the carrier with an organometallic compound before the treatment with the transition metal compound containing no chlorine. Examples of the chlorine compounds containing no transition metal as also of the organometallic compounds have been given above.

The present invention also related to the use of a procatalyst composition according to the invention in homo- and co-polymerization of olefins, wherein the polymerization is carried out by the aid of the said procatalyst composition and some organometallic co-catalyst compound of a metal belonging to the groups IA-IIIA of the periodic table of the elements. The co-catalyst compound is preferably an organometallic compound of aluminum such as a trialkylaluminum, most preferably triethylaluminum.

In addition to the procatalyst composition and the co-catalyst also a so called external electron donor can be used in the polymerization.

The invention is explained in the following by some examples.

Preparation of the catalyst

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Example 1

A. Impregnation of the carrier

1.0 g of silica which had been dried at 150°C for 4 hrs,

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300 mg of anhydrous magnesium dichloride, 0.36 mL of titanium tetrabutoxide, 0.88 mL of n-butanol and 10 mL of n-heptane were added in this order while stirring to a bottle equipped with a septum. When all the materials had been added, the bottle was sealed and the mixture was stirred at 25°C for 30 min and at 125°C in a bath for 4 hrs. The mixture was dried at 125°C in a bath for 20 min. 1.976 g of a free flowing powder was obtained containing 16.1 wt% of butanol and 2.6 wt% of titanium.

B. Treatment with TEA/EADC

The product of step A was suspended in 5 mL of n-pentane. 7.0 mL of a 10 wt% solution of triethyl aluminum (TEA) in pentane and 4.0 mL of a 10 wt% solution of ethyl aluminum dichloride (EADC) in pentane were added to the mixture while stirring. The mixture was stirred at 40°C in a bath for 20 min and dried in a stream of gaseous nitrogen for 45 min. The yield was 2.621 g containing 2.4 wt% Ti, 2.8 wt% Mg, 6.8 wt% Al and 14.6 wt% Cl. The dried procatalyst was stirred for further 15 hrs at room temperature, washed 3 times with 10 mL of n-heptane and dried in a stream of gaseous nitrogen for 20 min.

The composition of the catalyst was: Ti 3.5 %, Mg 4.1 %, Al 2.2 %, Cl 15.9 %.

Example 2

A. Treatment of the carrier with hexamethyldisilazane

To 2.0 g of silica which had been dried for 4 hrs at 150°C 15 mL of n-heptane and 0.6 mL of hexamethyldisilazane (HMDS) were added. The mixture was boiled at 50°C in a bath for 60 min and dried at the same temperature in a stream of gaseous nitrogen for 20 min.

B. Impregnation of the carrier

995 mg of the above prepared hexamethyldisilazane-treated silica, 300 mg of magnesium dichloride, 10 mL of n-heptane, 0.36 mL of titanium tetrabutoxide and 0.88 mL of n-butanol

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were added in this order to a bottle provided with a septum. When all the materials had been added, the bottle was sealed and the mixture stirred at 120°C in a bath for 4 hrs and dried at the same temperature in a stream of gaseous nitrogen for 20 min. The yield was 1.76 g.

C. Treatment with TEA/EADC

The product of step B was suspended in 5 mL of n-pentane. 6.3 mL of a 10 wt% solution of TEA in pentane and 3.4 mL of a 10 wt% solution of EADC in pentane were added. The mixture was stirred at room temperature for 20 min and dried in a stream of gaseous nitrogen for 45 min. The dried procatalyst was stirred for further 16 hrs at room temperature, washed 3 times with 10 mL of n-pentane and dried in a stream of gaseous nitrogen for 20 min.

The composition of the catalyst was: Ti 3.3 %, Mg 4.7 %, Al 2.8 %, Cl 18.5 %.

20 Example 3

A. Preparation of the pre-mixture

300 mg of anhydrous magnesium dichloride were suspended in 10 mL of n-heptane. 0.36 mL of titanium tetrabutoxide and 0.88 mL of n-butanol were added to the slurry. The mixture was stirred at 120°C in a bath for 4 hrs in order to dissolve the material completely.

B. Impregnation of the hexamethyldisilazane-treated carrier

The pre-mixture solution was transferred by siphonation into 995 mg of in example 2A prepared, hexamethyldisilazane-treated silica while stirring well. The mixture was dried in a flow of gaseous nitrogen at 120°C in a bath for 20 min. 1.66 g of a free flowing powder was obtained containing 24.3 wt% of butanol.

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C. Treatment with TEA/EADC

1.527 g of the above obtained product were suspended in 5 mL of n-pentane. 5.5 mL of a 10 wt% solution of TEA in

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pentane and 3.0 mL of a 10 wt% solution of EADC in pentane were added to the slurry. The mixture was stirred for 20 min at room temperature and dried in a stream of gaseous nitrogen for 45 min. The dried procatalyst was stirred for
5 further 15 hrs at room temperature, washed 3 times with 10 mL of pentane and dried in a stream of gaseous nitrogen for 20 min.

The composition of the catalyst was: Ti 3.1 %, Mg 4.6 %, Al 2.2 %, Cl 19.6 %.

Example 4

A. Preparation of the pre-mixture

386 mg of anhydrous magnesium dichloride were suspended in
15 12 mL of n-heptane. 0,5 mL of titanium tetrabutoxide and 1.22 mL of n-butanol were added to the slurry. The mixture was stirred at 125°C in a bath for 2½ hrs in order to dissolve the material completely.

B. Impregnation of the silica with the pre-mixture

The pre-mixture solution was transferred by siphonation into 3.0 g of silica which had been dried at 150°C for 4 hrs, while stirring well. The mixture was dried in a flow of gaseous nitrogen at 125°C for 15 min, whereby 4.4 g of a
25 free flowing powder was obtained, containing 18.5 wt% of butanol, 1.7 wt% of titanium and 2.0 wt% of magnesium.

C. Treatment with TEA/EADC

1.0 g of the above prepared procatalyst were suspended in
30 4 mL of n-pentane. 3.1 mL of a 10 wt% solution of TEA in pentane and 1.4 mL of a 10 wt solution of EADC in pentane were added to the slurry. The mixture was stirred at room temperature for 20 min, dried in a stream of gaseous nitrogen for 30 min and stirred further as dry at room temperature for 16½ hrs.

The composition of the catalyst was: Ti 1.2 %, Mg 1.5 %, Al 5.5 %, Cl 9.7 %.

Example 5A. Treatment of the carrier with hexamethyldisilazane

To 3.0 g silica (Davison 955) 15 mL of n-pentane and 1.35 mL of hexamethyldisilazane were added. The mixture was
5 boiled at 50°C in a bath for 60 min and dried at the same temperature for $\frac{1}{2}$ hr, whereby a dry, free flowing carrier powder was obtained.

B. Preparation of the pre-mixture

10 386 mg of anhydrous magnesium dichloride were suspended in 7 mL of toluene. 0.5 mL of titanium tetrabutoxide and 1.0 mL of n-butanol were added to the slurry. The mixture was stirred at 120°C in a bath for 3 hrs in order to dissolve the material completely.

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C. Impregnation of the carrier with the pre-mixture

The pre-mixture solution was transferred by siphonation into hexamethyldisilazane-treated carrier while stirring well. The mixture was dried in a flow of gaseous nitrogen at 80°C
20 in a bath for 30 min, whereby a dry, free flowing powder was obtained containing 20.3 wt% of butanol, 1.1 wt% of titanium and 1.8 wt% of magnesium.

D. Treatment with TEA/EADC (= example 5a)

25 1,0 g of the above prepared procatalyst were suspended in 3 mL of n-pentane. 4.1 mL of a 10 wt% solution of TEA in pentane and 1.1 mL of a 10 wt% solution of EADC in pentane were added to the slurry. The mixture was stirred at room temperature for 20 min, dried in a flow of gaseous nitrogen
30 for 20 min and stirred further as dry at room temperature for 16 hrs.

The composition of the catalyst was: Ti 1.3 %, Mg 1.6 %, Al 7.9 %, Cl 8.2 %.

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D. Treatment with TEA/DEAC (= example 5b)

1,0 g of the procatalyst prepared in step C were suspended in 3 mL of n-pentane. 4,1 mL of a 10 wt% solution of TEA

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in pentane and 2,1 mL of a 10 wt% solution of diethyl aluminum chloride (DEAC) in pentane were added to the slurry. The mixture was stirred at room temperature for 20 min, dried in a flow of gaseous nitrogen for 20 min and stirred
5 further as dry at room temperature for 16 hrs.

The composition of the catalyst was: Ti 1.2 %, Mg 1.5 %, Al 7.1 %, Cl 7.5 %.

10 Example 6

A. Treatment of the carrier with hexamethyldisilazane

To 1,1 g of silica 5 mL of n-pentane and 0.2 mL of hexamethyldisilazane were added. The mixture was boiled at 50°C in a bath for 60 min and dried at the same temperature for
15 $\frac{1}{2}$ hr, whereby a dry, free flowing carrier powder was obtained.

B. Impregnation of the carrier

To 1.06 g of the above prepared HMDS-treated silica 320 mg of anhydrous magnesium chloride, 5.0 mL of n-butanol and
20 0.36 mL of titanium tetrabutoxide were added in this order while stirring to bottle equipped with a septum. When all the materials had been added, the bottle was sealed and the mixture was stirred at 120°C in a bath for 4 hrs. The
25 mixture was dried at the same temperature in a stream of gaseous nitrogen for 3 hrs, whereby a free flowing powder was obtained containing 15.6 wt% of butanol and 3.0 wt% of titanium.

30 C. Treatment with DEAC

200 mg of the above obtained product were suspended in 0.5 mL of n-pentane. 0.94 mL of a 10 wt% solution of DEAC in pentane was added to the mixture and the mixture was stirred at room temperature for 20 min, at 45°C in a bath for 1 hr
35 and dried at 45°C in a bath with a stream of gaseous nitrogen for 20 min.

The composition of the catalyst was: Ti 2.5 %, Mg 3.6 %, Al 4.8 %, Cl 17.4 %.

Example 7

5 A. Treatment of the carrier with hexamethyldisilazane

To 3.0 g of silica (Davison 955) which had been dried at 200°C for 4 hrs, 15 mL of n-pentane and 0.8 mL of hexamethyldisilazane were added. The mixture was boiled at 50°C in a bath for 60 min and dried at the same temperature in
10 a stream of gaseous nitrogen for 20 min.

B. Preparation of the pre-mixture

386 mL of anhydrous magnesium dichloride were suspended in 12 mL of toluene. 0.5 mL of titanium tetrabutoxide and 1.0
15 mL of n-butanol were added to the slurry. The mixture was stirred at 120°C in a bath for 5½ hrs in order to dissolve the material completely.

C. Impregnation of the carrier with the pre-mixture

20 The pre-mixture solution was transferred by siphonation into the carrier while stirring well. The mixture was dried in a flow of gaseous nitrogen at 80°C in a bath for 45 min, whereby a free flowing powder was obtained containing 18.1 wt% of butanol, 1.2 wt% of titanium and 1.7 wt% of mag-
25 nesium.

D. Treatment with TEA/EADC

0.5 g of the above prepared procatalyst were suspended in 1.5 mL of n-pentane. 2.17 mL of a 10 wt% solution of TEA
30 in pentane and 0.5 mL of a 10 wt% solution of EADC in pentane were added to the slurry. The mixture was stirred at room temperature for 20 min, dried in a flow of gaseous nitrogen for 20 min and stirred further as dry for 16 hrs.

35 The composition of the catalyst was: Ti 0.98 %, Mg 1.5 %, Al 6.6 %, Cl 8.4 %.

Example 8A. Treatment of the carrier with hexamethyldisilazane

To 3.0 g of silica (Davison 955) 15 mL of n-pentane and 1,35 mL of HMDS were added. The mixture was boiled at 50°C in a bath for 60 min and dried at the same temperature in a stream of gaseous nitrogen for $\frac{1}{2}$ hr, whereby a dry, free flowing carrier powder was obtained.

B. Preparation of the pre-mixture

322 mg of anhydrous magnesium dichloride, 1.0 mL of n-butanol and 7.0 mL of toluene were stirred in a bottle equipped with a septum at 120°C in a bath for 3 hrs in order to dissolve the material completely. 0.4 mL of titanium tetrabutoxide was added to the solution, and the mixture was stirred at 120°C in a bath for 15 min.

C. Impregnation of the carrier with the pre-mixture

The pre-mixture solution was transferred by siphonation into the carrier while stirring well. The mixture was dried in a flow of gaseous nitrogen at 80°C in a bath for $\frac{1}{2}$ hr, whereby a free flowing powder was obtained containing 16.5 wt% of butanol, 1.5 wt% of titanium and 1.5 wt% of magnesium.

D. Treatment with TEA/EADC

1,0 g of the above prepared procatalyst were suspended in 3 mL of n-pentane. 3,96 mL of a 10 wt% solution of TEA in pentane and 1.16 mL of a 10 wt% solution of EADC in pentane were added to the slurry. The mixture was stirred at room temperature for 20 min, dried in a flow of gaseous nitrogen for 20 min and stirred as dry for further 16 hrs.

The composition of the catalyst was: Ti 1.6 %, Mg 1.3 %, Al 5.8 %, Cl 7.3 %.

Example 9A. Preparation of the pre-mixture 1

3.9 g of anhydrous magnesium dichloride were suspended in

30 mL of n-pentane. 14.4 mL of dry ethanol was added to the slurry. The mixture was boiled at 105°C in a bath for 1½ hrs in order to dissolve the material completely.

5 B. Impregnation of the silica with the pre-mixture 1

12,0 g of silica (Davison 955) which had been activated at 800°C were added to the pre-mixture 1. The mixture was stirred for 10 min at 105°C in a bath and dried in a stream of gaseous nitrogen at the same temperature for 2 hrs. 17.95 g of a free flowing powder was obtained containing 16.8 wt% of ethanol.

C. Treatment with HMDS

To 8.975 g of the above prepared impregnated carrier 40 mL of n-pentane and 7,6 mL of hexamethyldisilazane were added. The mixture was stirred at 50°C in a bath for 1 hr, dried in a stream of gaseous argon at the same temperature for 2 hrs, washed twice at room temperature with 50 mL of pentane and dried by purging with argon for 20 min.

20

D. Preparation of the pre-mixture 2

386 mg of anhydrous magnesiumdichloride and 2,8 mL of titanium tetrabutoxide were stirred at 120°C in a bath for 1½ hrs in order to dissolve the material completely. 3 mL of n-pentane was added to the solution.

25

E. Impregnation of the carrier with the pre-mixture 2

The pre-mixture solution 2 was transferred by siphonation into 7.5 g of the product of step C, which remained a flowing powder during the whole addition. When all of the pre-mixture had been added, the catalyst was stirred as dry at room temperature for further 24 hrs.

30

F. Treatment with EADC

To 1 g of the above prepared procatalyst 2.8 mL of a 10 wt% solution of EADC in pentane were added. The mixture was stirred at room temperature for 20 min and dried in a stream of gaseous nitrogen.

35

The composition of the catalyst was: Ti 2.9 %, Mg 4 %, Al 4.3 %, Cl 21.3 %.

5 Example 10

A. Treatment of the silica with hexamethyldisilazane

 To 6.0 g of silica (Davison 955) which had been activated at 800°C 30 mL of n-pentane and 0.78 mL of hexamethyldisilazane were added. The mixture was stirred at 50°C in a bath
10 for 1 hr and dried at the same temperature in a stream of gaseous nitrogen for 20 min.

B. Preparation of the pre-mixture 1 and impregnation into the carrier

15 1.95 g of anhydrous magnesium dichloride and 57.5 mL of tetrahydrofuran were stirred at 80°C in a bath for 7.5 hrs in order to dissolve the material completely. The solution was transferred by siphonation into hexamethyldisilazane-treated silica while stirring well. The mixture was dried
20 at 80°C in a bath for 4 hrs 45 min, whereby a free flowing powder was obtained containing 21.8 wt% of tetrahydrofuran and 4.5 wt% of magnesium.

C. Preparation of the pre-mixture 2 and impregnation into the carrier

25 386 mg of anhydrous magnesium dichloride, 2.8 mL of titanium tetrabutoxide and 3 mL of n-pentane were stirred at 50°C in a bath for 18 hrs in order to dissolve the material completely. The solution was transferred by sifonation into
30 the carrier treated with the magnesiumdichloride-THF-solution, which carrier remained as a flowing powder during the whole addition. The procatalyst was stirred as dry at room temperature for further 24 hrs and it contained 15.3 wt% of THF, 4.2 wt% of magnesium, 2.8 wt% of titanium and 12.6
35 wt% of chlorine.

D. Treatment with EADC

To 1 g of the above prepared procatalyst 2.3 mL of a 10 wt% solution of EADC in pentane was added. The mixture was stirred at room temperature for 20 min and dried in a stream of gaseous nitrogen for 20 min.

The composition of the catalyst was: Ti 2.8 %, Mg 4.1 %, Al 2.9 %, Cl 18.9 %.

10 Example 11A. Treatment of the carrier with hexamethyldisilazane

3.0 g of silica (Davison 955) which had been activated at 600°C, 20 mL of n-pentane and 0.39 mL of hexamethyldisilazane were stirred at 50°C in a bath for 1 hr and dried at the same temperature in a stream of gaseous nitrogen for 30 min.

B. Preparation of the pre-mixture

320 mg of anhydrous magnesium dichloride, 0.36 mL of titanium tetrabutoxide and 7.0 mL of n-butanol were stirred at 110°C in a bath for 3 hrs in order to dissolve the material completely.

C. Impregnation of the carrier with the pre-mixture

25 The pre-mixture solution was transferred by siphonation into 2.505 g of the above prepared HMDS-treated silica. The mixture was stirred at 110°C in a bath for 1 hr and dried in a stream of gaseous argon at the same temperature for 3 hrs 45 min, whereby a free flowing powder was obtained containing 12.9 wt% of butanol, 1.3 wt% of titanium and 2.4 wt% of magnesium.

D. Treatment with TEA/EADC

35 1.024 g of the above prepared procatalyst were suspended in 3 mL of n-pentane. 2.50 mL of a 10 wt% solution of TEA in pentane and 1.2 mL of a 10 wt% solution of EADC in pentane were added to the slurry. The mixture was stirred at 45°C in a bath for 20 min and dried at the same

temperature for a stream of gaseous argon for 20 min. The catalyst was stirred as dry at room temperature for further 16 hrs.

- 5 The composition of the catalyst was: Ti 1.3 %, Mg 2.0 %, Al 4.8 %, Cl 9.6 %.

Example 12

A. Treatment of the carrier with hexamethyldisilazane

- 10 4.0 mL of hexamethyldisilazane were added to 2.0 g of silica while stirring well and the mixture was allowed to stand at room temperature for a week in a sealed bottle equipped with a septum. The mixture was suspended in 7.0 mL of n-heptane, stirred at 85°C in a bath for 15 min and dried at
15 the same temperature in a stream of gaseous nitrogen for 30 min.

B. Preparation of the pre-mixture

- 417 mg of anhydrous magnesium dichloride, 0.54 mL of titanium tetrabutoxide and 4.2 mL of ethanol were stirred
20 at 110°C in a bath for 20 min in order to dissolve the material completely.

C. Impregnation of the carrier with the pre-mixture

- 25 The pre-mixture solution was transferred by siphonation into 1.2 g of the above prepared HMDS-treated silica. The mixture was stirred at 110°C in a bath for 1 hr and dried in a stream of nitrogen at 100°C in a bath for 1 hr, whereby a free flowing powder was obtained containing 15.1 wt% of
30 ethanol, 3.3 wt% of titanium and 4.0 wt% of magnesium.

D. Treatment with DEAC

- 5,1 mL of a 10 wt% solution of diethylaluminum in pentane were added to 1 g of the above prepared procatalyst powder.
35 The mixture was stirred at 40°C in a bath for 4 hrs and dried at 45°C in a bath for 5 min.

The composition of the catalyst was: Ti 2.6 %, Mg 3.1 %, Al 4.8 %, Cl 9.6 %.

Al 7.8 %, Cl 20.3 %.

Example 13

A. Treatment of the carrier with triethylaluminum

5 To 6.0 g of silica which had been activated at 600°C 36 mL of n-pentane and 5.13 mL of a 10 wt% solution of triethylaluminum in pentane were added. The mixture was stirred at 50°C in a bath for 30 min and dried in a stream of gaseous nitrogen at the same temperature for 1/2 hr.

10

B. Preparation of the pre-mixture

1.36 mg of anhydrous magnesium dichloride, 60 mL of tetrahydrofuran and 1.53 mL of titanium tetraisopropoxide (TiPT) were stirred at 85°C in a bath for 30 min in order to dis-
15 solve the material completely.

C. Impregnation of the carrier with the pre-mixture

The pre-mixture solution was transferred by siphonation into 4.0 g of the above prepared carrier. The mixture was stirred
20 85°C in a bath for 1 hr and dried at the same temperature for 6 hrs 45 min. The dry, free flowing procatalyst powder contained 2.6 % of titanium and 15.9 % of tetrahydrofuran.

D. Treatment with DEAC

25 The treatment was carried out in the same way as in step D of example 12 except that 680 mg of the procatalyst and 2.52 mL of a 10 wt% solution of DEAC in pentane were used.

The composition of the catalyst was: Ti 2.3 %, Mg 3.3 %,
30 Al 5.3 %, Cl 16.6 %.

Polymerization

1. Homopolymerization of ethene

The catalysts prepared according to examples 1-10 were
35 polymerized in pentane as follows:

In a 3-L reactor 1.8 L of n-pentane treated with oxygen and moisture scavengers were added. Then 30-50 mg of proca-

talyst dissolved in a small amount of pentane were added to the reactor through a feeding funnel and the temperature was raised to 80°C. A 0.5-L reactor was pressurized with hydrogen to a pressure of 5 bars (e.g. 1* 10 bars). This amount of hydrogen was fed to the reactor together with the 10 wt% solution of triethylaluminum (TEA/Ti = 30-50 mol/mol) in pentane as a co-catalyst and gaseous ethene as the monomer. The total pressure was raised to 15 bars with ethene, the temperature was raised to 90°C, and the polymerization was continued for 60 min. Ethene was continuously fed into the reactor in order to keep the pressure constant.

The catalysts prepared according to examples 11-13 were polymerized in isobutane as follows:

In a 3-L reactor 1.8 L of isobutane treated with oxygen and moisture scavengers were added. Then 30-80 mg of the catalyst suspended in a small amount of pentane and 0.8-1.35 mL of a 10 wt% solution of TEA in pentane as a co-catalyst were added. The temperature was raised to 90°C (example 11) or 95°C (examples 12-13). A 0.5-L reactor was pressurized with hydrogen to a pressure of 5 bars and hydrogen was fed to the reactor together with gaseous ethene until the total pressure was 27 bars. The polymerization was continued for 1 hr and the total pressure was kept constant with a feed of ethene.

2. Co-polymerization of ethene

Co-polymerization of ethene and alpha-olefins was carried out in the same way as for the homo-polymerization except that the co-monomer (180 g of 1-butene) was added to the reaction medium (1.8 L of isobutane) immediately after the addition of co-catalyst.

The results of polymerization with catalyst components prepared according to the examples 1-13 are shown in the Table.

TablePolymerization results

5	Example	Activity		MI	MFR	BD
		kg/g cat.	kg/g Ti	(21.6)	(21/2)	kg/m ³
10	1	10.0	286	15.75	29.79	360
	1*	6.8	195	124.60	31.12	280
	2	7.9	241	11.55	32.94	230
	3	9.9	318	14.49	33.35	280
	4	4.4	368	17.00	30.49	290
	5a	5.5	426	17.55	26.50	330
	5b	6.1	510	13.56	29.60	300
15	6	5.4	217	8.06	28.79	270
	7	4.0	405	23.00	31.60	340
	8	4.1	257	8.20	31.70	220
	9	3.2	109	17.88	29.10	300
	10	4.0	141	14.58	29.80	300
20	11	2.3	178	5.21	29.18	240
	11*	2.5	189	34.00	27.00	226
	12	8.6	332	19.20	30.68	400
	13	6.8	302	11.70	26.10	350

11* : Polymerization medium isobutane, in others pentane.

25 1* : Hydrogen pressure in 0,5-L reactor 10 bars, in others 5 bars.

11* : Co-polymerization with 1-butene.

MI : Melt index

MFR : Melt flow ratio

30 BD : Bulk density

Claims

1. A procatalyst composition, which is suited for homo- and co-polymerization of olefins together with an organometallic co-catalyst compound belonging to a metal of some of the groups IA-IIIA of the periodic table of the elements, and in the preparation of which an inert, solid carrier, from which the surface hydroxyl groups optionally have been removed thermally or by reacting the carrier with a compound removing the hydroxyl groups, has been treated with
- 5 a) a magnesium halide compound,
b) one or several compounds of a transition metal belonging to the groups IVB or VB of the periodic table of the elements, which compounds dissolve said magnesium halide and contain no chlorine, and
- 10 c) an electron donor compound dissolving/suspending said magnesium halide compound in order to prepare a precursor product, characterized in that the precursor product, which is obtained from said steps a)-c), carried out at simultaneously or in an optional order of sequence, has additionally been treated with a chlorine compound containing
- 15 no transition metal, or with a mixture of said chlorine compound and an organometallic compound.
2. A procatalyst composition according to claim 1,
- 25 characterized in that the steps a)-c) have been carried out by impregnating to the carrier a mixture of said magnesium halide compound, said transition metal compound and said electron donor compound as a solution.
3. A procatalyst composition according to claim 1,
- 30 characterized in that steps a)-c) have been carried out by mixing the carrier, said magnesium halide compound, said transition metal compound and said electron donor compound with each other without a separate dissolution.
- 35 4. A procatalyst composition according to claim 1, characterized in that steps a)-c) have been carried out by impregnating first to the carrier an electron donor

solution/sludge of the said magnesium halide compound and thereafter a mixture of the magnesium compound and the transition metal compound as a solution.

- 5 5. A procatalyst composition according to claim 4, characterized in that the inert carrier has preferably been treated with hexamethyldisilazane before impregnating into it a mixture of the magnesium compound and the transition metal compound as a solution.
- 10 6. A procatalyst composition according to any of claims 1-5, characterized in that the magnesium halide compound is magnesium chloride.
- 15 7. A procatalyst composition according to any of claims 1-6, characterized in that the transition metal compound is a tetraalkyl titanate, preferably $\text{Ti}(\text{OET})_4$, $\text{Ti}(\text{OPr})_4$ or $\text{Ti}(\text{OBu})_4$.
- 20 8. A procatalyst composition according to any of claims 1-7, characterized in that the electron donor compound is an alkylester of a carboxylic acid, an aliphatic ether, a cyclic ether, an aliphatic ketone or an aliphatic alcohol.
- 25 9. A procatalyst composition according to claim 8, characterized in that the electron donor compound is tetrahydrofuran, ethyl acetate or ethanol, propanol or butanol.
- 30 10. A procatalyst composition according to any of claims 1-9, characterized in that the chlorine compound not containing transition metal is chosen from the group HCl , CCl_4 , SiCl_4 or an alkyl aluminum chlorine compound.
- 35 11. A procatalyst composition according to claim 10, characterized in that the alkyl aluminum compound is ethyl aluminum dichloride, diethyl aluminum chloride or ethyl aluminum sesquichloride.

12. A procatalyst composition according to any of claims 1-11, characterized in that the organometallic compound is chosen from the group trialkyl aluminum, metal alkyl such as butyllithium, and hexamethyldisilazane.

5

13. A method for preparation of a procatalyst composition according to any of the preceeding claims for homo- and co-polymerization of olefins together with an organometallic co-catalyst compound of a metal belonging to any of groups
10 IA-IIIA of the periodic system of the elements, in which method an inert, solid carrier, from which the surface hydroxyl groups have optionally been removed thermally or chemically by reacting the carrier with a compound removing hydroxyl groups, is treated with

15

a) a magnesium compound,
b) one or several compounds dissolving said magnesium halide of a transition metal belonging to group IVB or VB of the periodical table of the elements, which compounds dissolve said magnesium halide and contain no chlorine, and
20 c) an electron donor compound dissolving/suspending said magnesium halide compound, characterized in that said steps a)-c) are carried out at the same time or in an optional order of sequence, whereafter the thus obtained precursor product is additionally treated with a chlorine compound
25 containing no transition metal, or with a mixture of said chlorine compound and an organometallic compound.

14. A method according to claim 13, characterized in that the steps a)-c) are carried out by impregnating into the
30 carrier a mixture of said magnesium compound, said transition metal compound and said electron donor compound as a solution.

15. A method according to claim 13, characterized in that
35 steps a)-c) are carried out by mixing the carrier, said magnesium halide compound, said transition metal compound and said electron donor compound with each other without a separate dissolution.

16. A method according to claim 13, characterized in that steps a)-c) are carried out by impregnating to the carrier first an electron donor solution/sludge of said magnesium halide compound and thereafter a mixture of the magnesium compound and the transition metal compound as a solution.

17. A method according to claim 16, characterized in that before the treatment of the carrier with the mixture of the magnesium compound and the transition metal compound as a solution it is additionally treated with said organo-metallic compound, preferably hexamethyldisilazane.

18. A method according to any of claims 13-17, characterized in that the magnesium halide compound is magnesium dichloride.

19. A method according to any of claims 13-18, characterized in that the transition metal compound is a tetraalkyl titanate, preferably $\text{Ti}(\text{OEt})_4$, $\text{Ti}(\text{OPr})_4$ or $\text{Ti}(\text{OBu})_4$.

20. A method according to any of claims 13-19, characterized in that the electron donor compound is an alkylester of a carboxylic acid, an aliphatic ether, a cyclic ether, an aliphatic ketone or an aliphatic alcohol.

21. A method according to claim 20, characterized in that the electron donor compound is tetrahydrofuran, ethyl acetate or ethanol, propanol or butanol.

22. A method according to any of claims 13-21, characterized in that the chlorine compound not containing transition metal is chosen from the group HCl , CCl_4 , SiCl_4 or an alkyl aluminum chlorine compound.

23. A method according to claim 22, characterized in that the alkyl aluminum compound is ethyl aluminum dichloride, diethyl aluminum chloride or ethyl aluminum sesquichloride.

24. A method according to any of claims 13-23, characterized in that the organometallic compound is chosen from the group trialkylaluminum, metal alkyl such as butyllithium and hexamethyldisilazane.

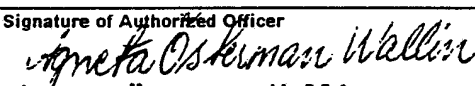
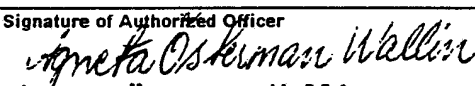
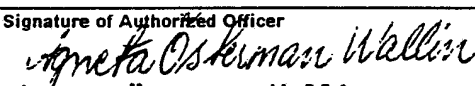
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25. The use of a procatalyst composition according to any of claims 1-12 together with a co-catalyst based on an organometallic compound belonging to groups IA-IIIA of the periodic table of the elements for homo- or co-polymerization of olefins.

10

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 91/00111

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 F 4/02														
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 5px;">Minimum Documentation Searched⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">Classification System</th> <th style="width: 80%;">Classification Symbols</th> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 08 F</td> </tr> </table> <div style="text-align: center; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div> <p style="margin-top: 10px;">SF,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	C 08 F								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">EP, A2, 0296561 (PHILLIPS PETROLEUM COMPANY) 28 December 1988, see page 3, line 12 - line 13; page 3, line 39 - line 40; page 4, line 43 - line 48; page 4, line 57 - page 5, line 4 --</td> <td style="vertical-align: top; text-align: center;">1-11,13-23,25</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">US, A, 4888318 (ALLEN ET AL) 19 December 1989, see column 5, line 7 - column 6, line 7; column 6, line 67 - column 7, line 2 --</td> <td style="vertical-align: top; text-align: center;">1-11,13-23,25</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">US, A, 4302566 (KAROL ET AL) 24 November 1981, see column 5, line 50 - column 6, line 50 --</td> <td style="vertical-align: top; text-align: center;">1-11,13-23,25</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	EP, A2, 0296561 (PHILLIPS PETROLEUM COMPANY) 28 December 1988, see page 3, line 12 - line 13; page 3, line 39 - line 40; page 4, line 43 - line 48; page 4, line 57 - page 5, line 4 --	1-11,13-23,25	Y	US, A, 4888318 (ALLEN ET AL) 19 December 1989, see column 5, line 7 - column 6, line 7; column 6, line 67 - column 7, line 2 --	1-11,13-23,25	Y	US, A, 4302566 (KAROL ET AL) 24 November 1981, see column 5, line 50 - column 6, line 50 --	1-11,13-23,25
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search 10th July 1991 </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report 1991 -07- 18 </td> </tr> <tr> <td style="width: 50%; padding: 5px;"> International Searching Authority <div style="text-align: center; margin-top: 10px;">SWEDISH PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;">  Agheta Österman Wallin </div> </td> </tr> </table>			Date of the Actual Completion of the International Search 10th July 1991	Date of Mailing of this International Search Report 1991 -07- 18	International Searching Authority <div style="text-align: center; margin-top: 10px;">SWEDISH PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;">  Agheta Österman Wallin </div>								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 4833111 (THOMAS E. NOWLIN) 23 May 1989, see abstract; claims 1-66 --	1-11,13- 23,25
Y	WO, A1, 8403888 (UNION CARBIDE CORPORATION) 11 October 1984, see claim 1 --	1-11,13- 23,25
Y	US, A, 4562168 (CLIFFORD C. LEE) 31 December 1985, see column 2, line 18 - line 32; column 3, line 1 - line 23; column 5, line 57 - line 64; abstract -- -----	1-11,13- 23,24

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 91/00111

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 91-05-29
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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		US-A-	4855271	89-08-08
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		AU-D-	4565879	79-10-04
		CA-A-	1143897	83-03-29
		EP-A-B-	0004645	79-10-17
		JP-C-	1334429	86-08-28
		JP-A-	54154488	79-12-05
		JP-B-	61000363	86-01-08

US-A- 4833111	89-05-23	AU-D-	2852889	89-07-20
		EP-A-	0324588	89-07-19
		JP-A-	1247401	89-10-03

WO-A1- 8403888	84-10-11	AU-B-	579996	88-12-22
		AU-D-	2618884	84-10-04
		CA-A-	1219400	87-03-17
		EP-A-B-	0120503	84-10-03
		JP-C-	1434534	88-04-07
		JP-A-	59230011	84-12-24
		JP-B-	62044004	87-09-17

US-A- 4562168	85-12-31	CA-A-	1243658	88-10-25
		EP-A-	0164596	85-12-18
		JP-A-	61081407	86-04-25